THERMAL DIFFUSION IN LIQUIDS

BY

DONALD JAMES TREVOY

B.S., University of Saskatchewan, 1944
M.S., University of Saskatchewan, 1946

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING
IN THE GRADUATE COLLEGE OF THE
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Introduction

Thermal diffusion in the liquid phase was first observed by Ludwig (L1) in 1856. When a temperature gradient was maintained in a uniform aqueous solution of sodium sulfate he found that a concentration gradient was established. Later Soret (S1) discovered the effect independently, and as a result thermal diffusion in the liquid phase is now termed the Ludwig-Soret or the Soret effect.

In liquids and liquid mixtures a simple theory of binary collisions is not sufficient to describe the molecular behaviour because the molecules are closely packed and are probably influenced by several neighbors simultaneously. Due to the complexity of the problem a complete mathematical theory of the liquid state has not yet been realized. It is possible, however, that thermal diffusion data for liquids may yield more specific information about the liquid state than the other transport properties as has been the case for gases. On this premise thermal diffusion has been adopted as the tool in a study of liquid mixtures.

The present work is confined to a study of the Soret effect in binary mixtures of unreactive hydrocarbons which form almost ideal solutions. It is desired to discover what fundamental properties of the pure compounds determine the magnitude and direction of the thermal diffusion constant. As a necessary adjunct to the work an extensive experimental investigation of ordinary diffusion and viscosity is included.

Kinetic Theory Of Thermal Diffusion

In the absence of an adequate kinetic theory of liquids we shall now postulate a relation for the prediction and correlation of thermal diffusion constants. Let us first consider a binary liquid mixture where only a mass difference between the molecules occurs. We shall suppose that an average speed

can be associated with molecules in the liquid phase and that this speed increases with increasing temperature. Considering only kinetic energy at constant temperature the average speed of molecules with different masses is different and the momentum is proportional to the square root of the mass. When a uniform liquid mixture is subjected to a temperature gradient there results a net velocity in the direction of lower temperature which establishes the density gradient. The heavy molecules having greater momentum are less easily stopped by collision and are carried further into the low temperature region than the light molecules. It is therefore expected that in liquids the species with greater mass will preferentially migrate to the cold wall.

Superimposed on the molecular weight effect will be a steric effect. Due to the close packed structure of molecules in a liquid, movement will be affected by the size and shape of the molecules. We shall now consider a binary liquid mixture where the mass is constant but the size of the molecule varies. The temperature gradient gives rise to a density gradient by causing a net velocity of both species in the direction of lower temperature. But due to the greater size of one species and to the relative inflexibility of the molecular cages in the low temperature region the large molecules are hindered more than the small ones in leaving this region. The net result is thus a migration of the larger species to the cold wall.

Since both the size and the mass cause migration in the same direction we shall define for each molecular species a cross-section σ effective in determining the direction and extent of thermal diffusion

$$\sigma = m\chi \tag{1}$$

This cross-section is the product of the mass and a quantity χ which is the area necessary to allow movement of a molecule, the area being in a plane perpendicular to the direction of motion of the molecules. The probability of separation by thermal diffusion will be proportional to the difference between the inverse cross-sections. Integrating all other effects in a

universal dimensional constant K and a factor f for deviation from ideality we obtain for the thermal diffusion constant

$$\left(\alpha = \mathrm{Kf}\,\frac{1}{\sigma_1} - \frac{1}{\sigma_2}\right) \tag{2}$$

We arbitrarily assign subscript 1 to the species with smaller mass. In accord with the above discussion regarding the effect of molecular mass on the direction of thermal diffusion we shall consider that a positive α corresponds to a movement of the heavy molecule to the cold wall and a negative α corresponds to a movement of the heavy molecule to the hot wall.

Phenomenological Theory Of Thermal Diffusion Column

Following the phenomenological treatment of Furry, Jones and Onsager (F1) and Jones and Furry (J2) we use average values for the temperature dependent quantities ρ, η, λ and D except in computing the convection velocity. The coefficient of thermal diffusion D_T is defined by the equation of diffusion

$$c_1\left(\vec{v}_1 - \vec{v}\right) = -\,D\ \mathrm{grad}\ c_1 - \frac{D_T}{T}\,\mathrm{grad}\ T \tag{3}$$

In the case of gases it has been shown that the coefficient of thermal diffusion is proportional to the product c_1c_2, and therefore a thermal diffusion constant α is introduced and defined by the relation

$$D_T = Dc_1c_2\alpha \tag{4}$$

In terms of α equation (3) becomes

$$c_1\left(\vec{v}_1 - \vec{v}\right) = D\left(-\,\mathrm{grad}\ c_1 - \alpha\, c_1\, c_2\,\mathrm{grad}\ \ln T\right) \tag{5}$$

We shall consider the case of two flat parallel vertical plates connected to reservoirs above and below, the plates being maintained at temperatures T_H and T_C where $T_H > T_C$. The trans-

port equation derived by Furry, Jones and Onsager is

$$\ln q_e = \left[\frac{63\,\alpha\,D\,\eta\,L}{2\,\overline{T}\,w^4\,\beta\,g}\right]\left[\frac{1}{1+5670\left(\frac{\eta D}{g w^3 \beta \Delta T}\right)^2}\right] \quad (6)$$

where the separation factor, q, is defined by

$$q = \left(\frac{c_1}{c_2}\right)_{Top}\left(\frac{c_2}{c_1}\right)_{Bottom} \quad (7)$$

Experimental Methods And Results

Most of the thermal diffusion measurements were made on a concentric tube column, although attempts were also made to develop a convection-free diaphragm cell for measuring thermal diffusion constants. Chemicals having a purity of about 99 mole % were used and samples were compared in a Zeiss water interferometer. The significant dimensions of the column in c.g.s. units were

$$w = 0.0508$$
$$L = 10.16$$
$$V_+ = 8.47$$
$$B = 6.32$$

The outer tube was cold-rolled steel with reservoirs silver-soldered to each end before lapping. The inner tube was separated from the outer by piano wire spacers soldered to a wire ring in each reservoir. Special brass valves with very small holdup were provided for draining the contents of column and reservoirs. The column was mounted in a water thermostat, and water from a second thermostat was circulated through the inner tube at a velocity of about 5 feet per second by a positive displacement pump. Bath temperatures were regulated to better than 0.1°C, and runs usually lasted from 4 to 10 hours. The contents of the column and reservoirs were drained into three 50 ml. erlenmeyer flasks at the end of each run.

Two series of binary mixtures were studied: benzene-n-

paraffin and n-paraffin-n-paraffin hydrocarbons. The effect of replacing one of the n-paraffin hydrocarbons by an i-paraffin having the same number of carbon atoms was also measured in some instances. The concentration of all mixtures was initially 50 mole % and in most runs the ΔT was about 5°C.

For the measurement of diffusion coefficients a diaphragm cell was used. It consisted of a fine pyrex fritted disc having a diameter of 30 mm. which separated two reservoirs with volumes of 23 ml. Capillary tubes were provided to facilitate filling and sampling. The cell was suspended in a water thermostat and the temperature was regulated to within 0.02°C. The recommended technique of first establishing approximately the correct concentration gradient in the disc before beginning an experiment was followed throughout the work. The cell was calibrated with pure water vs 0.1N HCl using the value 2.90×10^{-5} cm.^{2}/sec. for the integral diffusivity at 25°C. (J1, G2). In all cases it was desired to determine the differential diffusion coefficient for a 50 mole % solution. The concentrations of initial solutions varied between 45 - 55 and 48 - 52 mole % depending on the difference in refractive indices of the components. Runs lasted from 12 to 36 hours and were carried out in duplicate at each of the three temperatures. Average values of the diffusion coefficient are presented in Table I, and were calculated by the equation of Gordon (G2).

Values for the kinematic viscosity were determined at three temperatures with 50 mole % mixtures using viscometers of the Cannon-Fenske-Ostwald type. The viscometers were immersed in water thermostats regulated to 0.01°C. and efflux times were measured three or four times at each temperature with an electric timer. For calculation of absolute viscosities the densities of mixtures were calculated from data for pure compounds by assuming no change in volume on mixing.

Diffusion and viscosity data were interpolated and extended by using plots of log D or log η vs 1/T which yielded substantially straight lines. Values of β for mixtures were calculated from data for pure compounds by assuming no change in volume on mixing.

TABLE I. Diffusion coefficients for 50 mole % liquid mixtures.

Mixture	Diffusion Coefficient, 10^5D 25°C.	45°C.	65°C.
Ph — n-C_7	2.47	3.40	4.32
Ph — n-C_{10}	1.72	2.51	3.10
Ph — n-C_{12}	1.40	—	—
Ph — n-C_{16}	0.96	—	—
Ph — n-C_{18}	0.86	—	—
n-C_7 — n-C_{12}	1.58	2.14	2.69
n-C_7 — n-C_{14}	1.29	—	—
n-C_7 — n-C_{16}	1.00	1.44	2.05
n-C_7 — n-C_{18}	0.92	—	—
i-C_7 — n-C_{12}	1.44	—	—
i-C_7 — n-C_{18}	0.88	—	—
Ph — i-C_7	2.49	—	—

Average values of the thermal diffusion constant calculated by equation (6) are given in Table II.

TABLE II. Thermal diffusion constants obtained with a concentric tube column for 50 mole % liquid mixtures.

Mixture	$\overline{T}$ — 273	ΔT	α
Ph — n-C_7	23	5.4	— 1.19
	33	5.4	— 1.20
	33	10.8	— 1.24
	33	16.4	— 1.28
	48	5.0	— 1.06
	63	5.0	— 1.14
Ph — n-C_{10}	23	5.5	— 0.22
	33	5.5	— 0.41
	48	5.5	— 0.44
	63	5.5	— 0.47
	78	5.4	— 0.68
Ph — n-C_{12}	33	5.3	— 0.31
Ph — n-C_{14}	33	5.3	— 0.21
Ph — n-C_{16}	33	5.4	— 0.01

Mixture	$\overline{T} - 273$	ΔT	α
Ph — n-C_{18}	33	5.4	+ 0.07
n-C_7 — n-C_{12}	23	5.4	0.57
	33	5.4	0.61
	48	5.4	0.54
	63	5.3	0.56
	78	5.2	0.44
n-C_7 — n-C_{14}	33	5.2	0.90
	36	10.2	0.88
	48	6.4	0.93
	63	6.5	1.08
n-C_7 — n-C_{16}	33	5.3	1.03
n-C_7 — n-C_{18}	33	5.3	0.95
i-C_7 — n-C_{12}	33	5.4	0.43
i-C_7 — n-C_{16}	33	5.4	0.22
Ph — i-C_7	33	5.3	— 0.59

Correlation And Discussion Of Results

As predicted by (6) for our choice of column and operating variables α is substantially independent of ΔT. A study of Table II shows this to be true for benzene—n-heptane mixtures over a three-fold range of ΔT, and for n-heptane—n-tetradecane over a two-fold range.

While the data for each system are consistent, within experimental error, α increases slightly with increasing temperature in some cases and decreases slightly in others. For this reason one cannot generalize regarding the dependence of α on temperature although it appears that α does not vary rapidly with temperature over a range of 55°C.

A test of equation (2), which considers the effect of molecular mass and size on the thermal diffusion constant, is also afforded by data given in Table II. In accordance with the view presented by Glasstone (G1) the n-paraffin hydrocarbons are considered to be zigzag chains of carbon atoms with a bond

angle of 109°28′. Values of χ were calculated from atomic diameters given by Glasstone. For $K = 9.13 \times 10^{-38}$ and $f = 1.20$ calculated values from equation (2) and experimental values of the thermal diffusion constant showed excellent agreement. It is noted that the thermal diffusion constant changes sign in the Ph—n-C_X series. The large negative value of α in the Ph—n-C_7 mixture indicates a greatly reduced mobility on the part of the benzene molecule as compared to that of a paraffin having the same number of carbon atoms. This unusually low mobility accounts in large part for the anomalous behaviour of benzene both as pure liquid and in mixtures. Such effects as the abnormally high viscosity of benzene and the deviations from Raoult's law of benzene solutions may well be due to the low mobility of the benzene moleclue.

Values of the diffusion coefficient are best correlated by the equation of Arnold (A1). The constant in his equation was altered from 0.0010 to 0.00161 and the abnormality factors were 1.00 and 1.33 for normal paraffin hydrocarbons and benzene, respectively. Values of the diffusion coefficient calculated by the equations of Stearn, Irish and Eyring (S2) are too high in all cases and no simple relation exists between observed and calculated values. It is concluded that the equations are of no practical values for calculating diffusivities.

Table Of Nomenclature

B — mean circumference, $\pi(r_1 + r_2)$, cm.
c_1 — mole fraction of component one; $c_1 + c_2 = 1$
D — coefficient of ordinary diffusion, cm.^{2}/sec.
D_T — coefficient of thermal diffusion, cm.^{2}/sec.
f — factor of deviation from ideality; cf. Eq. (2).
g — acceleration of gravity, cm./sec.^{2}.
K — cf. Eq. (2).
L — length of column, cm.
m_1 — mass of a molecule of component one, gm.
q — separation factor, cf. Eq. (7).

q_e — equilibrium separation factor.
T — temperature, °A.
T_C — temperature of outer tube or cold wall, °A.
T_H — temperature of inner tube or hot wall, °A.
ΔT — $T_H - T_C$, °A.
$\overline{T}$ — average temperature, $\frac{1}{2}(T_H + T_C)$, °A.
V_+ — volume of one reservoir, cm.^{3}.
$\vec{v}_1$ — convection velocity of component one.
$\vec{v}$ — convection velocity of fluid as a whole, $c_1\vec{v}_1 + c_2\vec{v}_2$.
w — one-half the distance between hot and cold walls, $\frac{1}{2}(r_1 - r_2)$, cm.
X — number of carbon atoms in hydrocarbon chain.
α — thermal diffusion constant, D_T/Dc_1c_2.
β — $-d\rho/dt$.
η — viscosity, poise.
λ — thermal conductivity, cal./cm.deg.sec.
ρ — density, gm./cm.^{3}.
σ — mass cross-section, gm.cm.^{2}.
χ — molecular cross-section. cm.^{2}.

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VITA

The author was born on January 27, 1922, in Saskatoon, Saskatchewan, Canada. He attended Westmount Public School and Bedford Road Collegiate Institute, both in Saskatoon. During this time he studied piano and theory and was made Associate of the Toronto Conservatory of Music in 1939. He then entered the University of Saskatchewan and graduated with great distinction in Chemical Engineering in 1944. Working in the laboratories of the National Research Council of Canada in Saskatoon he completed the master's thesis in 1946 and the degree was conferred in May by the University of Saskatchewan. He then joined the staff of the National Research Council of Canada, but left in September, 1946, upon admission to the Graduate School of the University of Illinois. He returned to Saskatoon for four months in 1947 to work with the National Research Council. During his academic career the author was awarded two undergraduate bursaries by the University of Saskatchewan, two graduate scholarships by the National Research Council of Canada, two graduate fellowships by the University of Illinois, and was twice appointed to the Shell Fellowship in Chemical Engineering at the University of Illinois.